

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Synthesis and performance of novel anion exchange membranes based on imidazolium ionic liquids for alkaline fuel cell applications

Jun Fang^{*}, Ming Lyu, Xin Wang, Yongbin Wu, Jinbao Zhao

Department of Chemical & Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

H I G H L I G H T S

- Novel anion exchange membranes based on two types of imidazolium ionic liquids were synthesized.
- The properties of the membranes could be tuned by varying the monomer ratios.
- The ionic conductivity of the synthesized membrane is as high as $2.26 \times 10^{-2} \text{ S cm}^{-1}$ at 30 °C.
- All the membranes show excellent thermal and chemical stability.
- A peak power density of 116 mW cm^{-2} of the H_2/O_2 fuel cell is obtained at 60 °C.

A R T I C L E I N F O

Article history:

Received 17 December 2014

Received in revised form

3 March 2015

Accepted 9 March 2015

Available online 11 March 2015

Keywords:

Anion exchange membrane

Fuel cell

Imidazole ionic liquid

Polymerization

A B S T R A C T

Novel anion exchange membranes (AEMs) based on two types of imidazolium ionic liquids, 1-vinyl-3-methylimidazolium iodide [VMI]I and 1-vinyl-3-butylimidazolium bromide [VBI]Br, have been synthesized by copolymerization. The obtained membranes are characterized in terms of water uptake, ion exchange capacity (IEC), ionic conductivity as well as thermal and chemical stability. The conductivity reaches 0.0226 Scm^{-1} at 30 °C. All the membranes show excellent thermostability. The membranes are stable in 10 mol L^{-1} NaOH solution at 60 °C for 120 h without obvious changes in ion conductivity. Fuel cell performance using the resulting membrane has been investigated. The open circuit voltage (OCV) of the H_2/O_2 fuel cell is 1.07 V. A peak power density of 116 mW cm^{-2} is obtained at a current density of 230 mA cm^{-2} at 60 °C. The results demonstrate the brilliant prospect of the developed membranes for alkaline fuel cell applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells, which directly convert chemical energy of fuel and oxidant to electricity, have been believed to provide clean and efficient energy sources for portable power applications and power plants [1–3]. As one of the critical component of fuel cell, the electrolyte membrane has a significant influence on cell performance. The proton exchange membrane fuel cells (PEMFCs) commonly using Nafion[®] membrane as electrolyte have been well developed during the past few decades. Despite Nafion[®] membrane presents excellent chemical and thermal stability and high proton conductivity, the commercialization of PEMFCs has been impeded for the high cost of noble metal catalysts and membranes, slow oxygen reduction kinetics, high methanol crossover (when Nafion[®]

membrane was used in direct methanol fuel cells) and complex water management [4–7].

Alkaline anion exchange membrane fuel cells (AEMFCs), using anion exchange membranes instead of proton exchange membranes, offer important benefits over their acidic counterparts (PEMFCs). The more facile kinetics of the oxygen reduction reactions in alkaline condition allow for the use of non-noble metal catalysts in AAEMFCs, such as silver, nickel, and palladium which on one aspect greatly reduced the cost of fuel cell devices [8,9]. As a crucial component in AEMFCs, the anion exchange membranes (AEMs) conduct hydroxide ions from cathode to the anode where water is produced, which can help simplify the water management. Moreover, the hydroxide ions move in the opposite direction with the fuel, which reduce fuel permeability and the cost on other aspects [10,11]. Although AEMFC is developed relatively later, it has become one of hot research topics in recent years. Various types of AEMs were obtained by chemical modification method from

^{*} Corresponding author.

E-mail address: jfang@xmu.edu.cn (J. Fang).

commercial available polymers, such as polyethersulfone cardo [12], poly (phthalazinon ether sulfone ketone) (PPESK) [13], polysulfone [14] and poly(arylene ether sulfone) [15]. Radio grafting method [16] and polymerization route [17,18] were also used to prepare AEMs. In many earlier studies, chloromethylation using chloromethyl ether, followed by quaternization process were unavoidable to prepared quarternized polymers. However, the chloromethylation reagents are considered to be highly toxic and carcinogenic. Furthermore, the alkyl quaternary ammonium groups on the side chain could be easily degraded due to nucleophilic substitution and (or) Hofmann elimination reaction, especially at high pH and elevated temperature [19].

To date, only a few reports about preparation of AEMs based on imidazolium ionic liquids (ILs) have been found [20,21]. In this work, we use the polymerizable ILs as the main materials to obtain AEMs for two reasons. One is that the polymerizable ILs provide $-C=C-$ for free radical copolymerization which effectively synthesize the target copolymers by controlling the monomer ratio in the reactants. The cationic group of the ILs can provide ionic conduction for AEMs as well, thus the synthesized polymers can transfer anion directly, which avoids the process of chloromethylation in the synthetic route. The other is that the imidazolium cations are more stable than the conventional quaternary alkyl ammonium cations at high pH and elevated temperature [22,23] due to the large π bond in the ILs. In this paper, novel AEMs based on 1-vinyl-3-methylimidazolium iodide and 1-vinyl-3-butylimidazolium bromide are reported. The properties of the synthesized AEMs have been investigated in terms of water uptake, ion exchange capacity (IEC), ionic conductivity as well as thermal and chemical stability.

2. Experimental

2.1. Materials

1-Vinylimidazole (99%) was purchased from Meryer (Shenzhen) Chemical Technology Co., Ltd. Iodomethane (MeI) was obtained from Shanghai Experiment Reagent Co., Ltd. 1-Bromobutane, styrene, 2,2'-azobisisobutyronitrile (AIBN) were business provided by China National Medicines Co., Ltd. 1-Vinylimidazole, 1-bromobutane, styrene were distilled under reduced pressure before use. AIBN was dissolved in boiled methanol, recrystallized at 0 °C, and then dried under vacuum at room temperature. The other chemicals were analytical grade and used as received. Deionized water was used throughout this work.

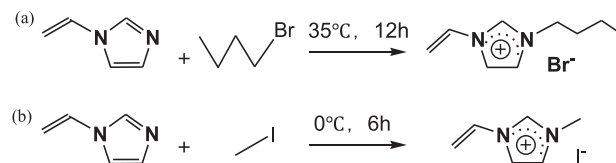
2.2. Synthesis of imidazolium ionic liquids

A mixture of 1-vinylimidazole (9.1 mL, 0.1 mol) and 1-bromobutane (10.8 mL, 0.1 mol) was added to a 100 mL three-neck flask and magnetically stirred at room temperature for 12 h under nitrogen protection. The liquid product [VBI]Br was extracted with chloroform and ethyl ether in order to remove the unreacted 1-bromobutane and 1-vinylimidazole, then, dried at room temperature for 6 h under vacuum.

A mixture of 1-vinylimidazole (9.1 mL, 0.1 mol) and methyl iodide (6.4 mL, 0.1 mol) was added to a 100 mL three-neck flask and magnetically stirred for 6 h under nitrogen protection in an ice bath. The liquid product [VMI]I was extracted by ethyl ether and dried at room temperature for 6 h under vacuum. The synthesis routes of [VBI]Br and [VMI]I are showed in Scheme 1.

2.3. Synthesis of copolymers

The reaction mixture containing [VBI]Br and styrene was added



Scheme 1. Synthesis routes of Ionic Liquids: (a) [VBI]Br (b) [VMI]I.

to a three-neck flask using 2,2'-azobisisobutyronitrile (AIBN) as an initiator (0.2 wt%) and ethanol (EtOH) as a solvent. The mixture was magnetically stirred at 65 °C for 24 h under nitrogen protection. After the copolymerization completed, the obtained yellowish solid was washed with ethyl ether for 3 times, again thoroughly washed with deionized water and dried in a vacuum oven at 65 °C for 6 h. After that, the solid product was washed by tetrahydrofuran and dried under vacuum at 65 °C overnight. Scheme 2 shows the schematic of the copolymerization of [VBI]Br and styrene. The copolymer samples of [VBI]Br and styrene with different feed ratios were labeled as copolymer A, B and C, respectively. The copolymerization of [VMI]I and styrene was carried out using the same method mentioned above and the schematic of the synthesis route is shown in Scheme 3. The copolymer samples of [VMI]I and styrene with different composition were labeled as copolymer D, E and F, respectively.

2.4. Preparation of membranes

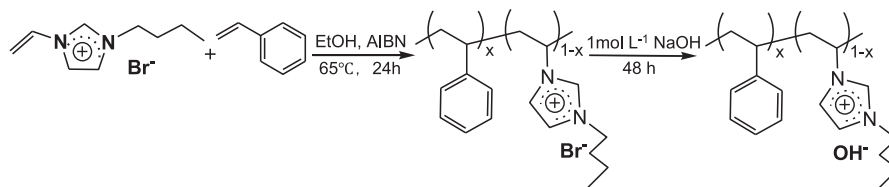
A certain amount of copolymers were dissolved in N,N-Dimethylformamide (DMF) respectively to form a 5–10 wt% solution. The solution was cast onto flat glass plates at room temperature, dried in a vacuum oven at 80 °C for 8 h after the deaeration process under vacuum continuing for 2 h to prepare membrane, respectively. The membranes that peeled off from the flat glass plates were kept in 1 mol L⁻¹ NaOH solution for 48 h. Finally, the membranes were washed thoroughly by deionized water to remove the residual NaOH and stored in deionized water for further use. The thickness of the dry anion exchange membranes were controlled between 30 and 60 μ m.

2.5. Characterization

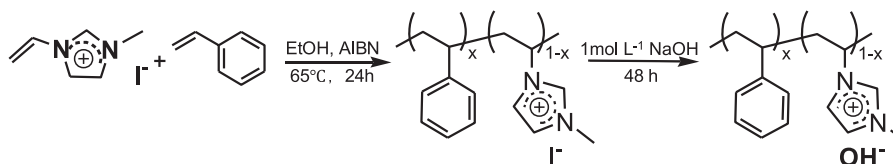
The Fourier Transform Infrared spectroscopy (FT-IR) spectra of [VBI]Br, [VMI]I, resulting copolymers were measured using a Nicolet FT-IR740SX spectrophotometer (Thermo Electron Corporation, USA) with a resolution 4 cm⁻¹. Elemental analyses were performed on a Vario EL III Elemental analyzer (Elementar Analysen System GmbH, Germany). Thermo-gravimetric analysis (TGA) was recorded using a TG209F1 system (NETZSCH, Germany) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 30 °C to 600 °C.

2.6. Water uptake

Water uptake was determined by measuring the variation in the weight of the OH⁻ form membrane before and after immersing in the deionized water. The OH⁻ form membrane was immersed in deionized water during 48 h at room temperature, and weighed immediately after removing the free water on the membrane surface with a piece of absorbent paper. Then the wet membranes were dried at 60 °C under vacuum until the constant weights were obtained. The water uptake was calculated by the following equation:



Scheme 2. Preparation of OH[−] form membrane based on [VBI]Br and Styrene.



Scheme 3. Preparation of OH[−] form membrane based on [VBI]I and Styrene.

$$WU(\%) = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where WU stands for the water uptake, W_w is the mass of the wet membrane, and W_d is the mass of the dry membrane.

2.7. Ion exchange capacity (IEC)

The IEC was measured by a standard back titration method. A piece of dry OH[−] form membrane was soaked in 0.1 mol L^{−1} HCl solution (25 mL, V_{HCl} , the volume for membranes soaking) at room temperature for 48 h. The solution was titrated with 0.1 mol L^{−1} NaOH solution (V_{NaOH} , the volume for the back titration). After that, the Cl[−] form membrane was dried at 60 °C under vacuum until the weight remained constant and measured. The calculation of IEC was based on the following equation:

$$IEC(\text{mmol g}^{-1}) = \frac{(V_{HCl} - V_{NaOH})}{W_d} \times C \quad (2)$$

where the C is the concentration of HCl and NaOH solutions, and W_d is the mass of dry Cl[−] form membrane.

2.8. Ionic conductivity

Ionic conductivity is one of the most important properties for electrolyte membrane. The hydroxyl conductivities of the OH[−] form membranes were measured by a two-electrode AC impedance method in a homemade cell. The cell was connected to a Parstat 263 electrochemical equipment (Princeton Advanced Technology, USA). The membrane sample was sandwiched between the two stainless steel electrodes and the resistance through the plane was measured, as described in our previous works [13,16,20,21]. The impedance spectrum was recorded in the frequency range from 0.1 Hz to 100 KHz. All the membrane samples were soaked in deionized water for at least 48 h before the test. The ionic conductivity can be calculated as follow:

$$\sigma = \frac{l}{R \times A} \quad (3)$$

where l (cm) is the distance between two potential sensing stainless steel electrodes, R (Ω) is the resistance of the membrane sample, and A (cm²) is the surface area of the membrane exposed to the electric field.

2.9. Chemical stability

Five OH[−] form membrane samples were immersed into 2, 4, 6, 8, 10 mol L^{−1} NaOH solutions at 60 °C for 120 h, respectively. The sixth sample was immersed into 1 mol L^{−1} NaOH solution for 120 h as a comparison. All the membrane samples were thoroughly washed by deionized water until the free NaOH inside the samples was completely removed. The ionic conductivities of six samples were tested at 30 °C to investigate the changes.

2.10. Membrane electrode assembly (MEA)

The membrane electrode assembly (MEA) is made up of an AEM and anode/cathode electrodes. In this study, membrane A was used as the AEM for the test. The anode/cathode electrodes consisted of anode/cathode catalyst layers (Pt/C, 40 wt% Pt, Johnson Matthey) and diffusion layers (Teflon-treated carbon paper, Toray-250). The ionomer solution (5 wt%) was prepared using the OH[−] form membrane A, which was mixed with the catalyst powder and isopropanol to prepare the catalyst ink for the electrode. The ink in which the weight ratio of catalyst to ionomer was 7:3, was stirred continuously for 24 h until the uniform mixture was obtained. Then the catalyst ink was sprayed onto the Teflon-treated carbon paper to prepare the resulting electrode with an active area of 2.5 × 2.5 cm² and a catalyst loading of 1 mg cm^{−2}. The AEM sandwiched between the anode and cathode electrodes was hot-pressed at 0.5 MPa for 5 min at 60 °C to obtain MEA for fuel cell test.

2.11. Fuel cell test

The MEA was assembled into a single fuel cell with serpentine flow channels. The flow rate of H₂/O₂ was 100 mL min^{−1}, and the humidification temperature increased with the test temperature, both of which were controlled by fuel cell test equipment (GEFC-10, Guangdong Electronic Technology Research Institute). The single cell test was performed at 60 °C with a humidity of 100% using an electronic load (ZY8714, ZHONGYING Electronic Co., Ltd).

3. Results and discussion

3.1. Preparation and the FT-IR spectrum of IILs and OH[−] form anion exchange membranes

The synthesis routes of imidazolium ionic liquids are shown in Scheme 1, and the details are described in Section 2.3. The reactions

could be readily carried out due to the strong nucleophilicity and steric accessibility of the number 3 position nitrogen atom in 1-vinylimidazole and high reactivity of 1-bromobutane and methyl iodide. Both [VBI]Br and [VMI]I are soluble in water, alcohols and DMF, insoluble in ethyl ether, chloroform and tetrahydrofuran.

The copolymers for preparing OH[−] form anion exchange membranes based on two types of imidazolium ionic liquid monomers were synthesized via free radical polymerization, as mentioned in Section 2.3. The synthetic routes are shown in Scheme 2 and Scheme 3. Because of the strong water affinity of imidazolium ionic liquids, styrene was introduced to the polymer backbone to adjust the hydrophilic-lipophilic balance of the membranes. The properties of the copolymers could be tuned by varying the monomer ratios in the reactants.

The feed ratio of IILs/styrene, nitrogen content of copolymers and the molar ratio of IILs/styrene in copolymers are summarized in Table 1. Sample A, B and C were polymerized by [VBI]Br with styrene, while Sample D, E and F were polymerized by [VMI]I with styrene. The Nitrogen only existed in the imidazolium cation groups, hence, the amount of imidazolium groups in the copolymers could be reflected by the nitrogen content and controlled by varying the feed ratio of IILs/styrene. It can be seen in Table 1 that the nitrogen content of copolymers decreased with the decreasing amount of ionic liquids. All the copolymers and OH[−] form anion exchange membranes obtained in this work are soluble in alcohols and DMF, insoluble in ethyl ether, chloroform and tetrahydrofuran. Thus, the membranes could be prepared by solution casting method mentioned in Section 2.4.

Fig. 1 shows the results of FT-IR spectra analysis of IILs and membranes. The strong peaks between 2800 and 3000 cm^{−1} are the characteristics of methyl and methane of the branch of imidazolium cation. The sharp peak at 1572 cm^{−1} is identified to the stretching vibration of C=N and the peak at 1162 cm^{−1} is identified to the flexural vibration of C–H in the imidazole ring.

The peaks appearing between 760 and 850 cm^{−1} in Fig. 1b and d confirm the presence of benzene ring. The peaks from 3000 to 3100 cm^{−1} represent the C–H of benzene ring. The strong absorption peak at 3400 cm^{−1} in the figure belongs to the stretch vibration of O–H. The results clearly confirm the successful synthesis of IILs and the OH[−] form anion exchange membranes.

3.2. Thermal analysis

The thermal stabilities of the developed membranes were evaluated using thermal gravimetric analysis (TGA). Fig. 2 shows the TGA curves of OH[−] form membrane A and D. The first slight weight loss (<1.5%) before 200 °C was suspected of the loss of residual water or organic solvent (such as DMF) in the samples. The second weight loss (30%) between 200 and 350 °C was considered to be caused by the degradation of the imidazole group [22]. The weight loss of membrane D before 300 °C was less than that of membrane A due to the less number of carbon atoms of alkyl in the imidazolium cation groups. The onset decomposition temperatures

Table 1
The synthetic conditions and the N content of copolymer samples.

Copolymer sample	Feed ratio of IILs/Styrene (mole)	N Content (wt%)	Molar ratio of IILs/Styrene in copolymer
A	[VBI]Br: Styrene = 1:1.5	6.674	1:1.8
B	[VBI]Br: Styrene = 1:2.0	5.681	1:2.5
C	[VBI]Br: Styrene = 1:2.5	4.646	1:3.5
D	[VMI]I: Styrene = 1:1.5	7.768	1:1.2
E	[VMI]I: Styrene = 1:2.0	7.337	1:1.4
F	[VMI]I: Styrene = 1:2.5	6.286	1:2.0

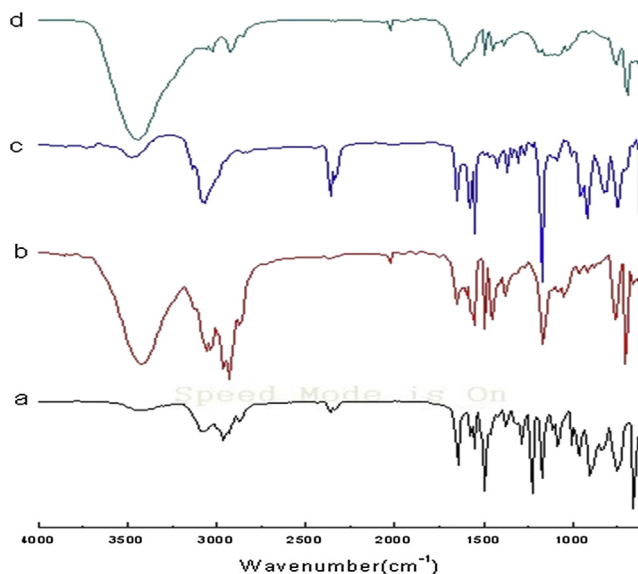


Fig. 1. The results of FT-IR spectra analysis of IILs and membranes.

in this region of membrane A and D were 282 °C and 350 °C respectively. The third weight loss started from 350 °C and was believed corresponding to the degradation of the main chain [24]. No significant weight loss is recorded below 200 °C, showing that the anion exchange membranes exhibit a thermotolerant temperature higher than 200 °C.

3.3. Water uptake and ionic exchange capacity

Table 2 lists the water uptake of the six OH[−] form membrane samples. The test method was described in Section 2.6. The water uptake of ionic exchange membranes reflects the hydrophilicity of the membranes because of the strong hydrophilicity of the imidazolium salt. Thus, it can be observed that the water uptake of the membrane increases with the increase of the imidazolium cation group content in the membrane. Membrane D shows a water uptake of 82.7% with the highest content of imidazolium cation groups.

Table 2 also lists the ionic exchange capacities of the six OH[−]

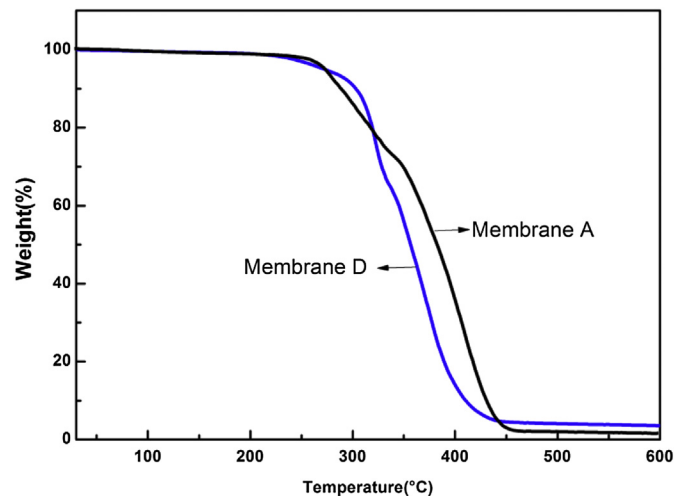


Fig. 2. Thermo Gravimetric analysis of membrane A and membrane D.

Table 2
Characterization of copolymers.

Membrane sample	Thickness (μm)	Water uptake (%)	IEC (mmol g^{-1})	σ at 30 °C ($10^{-2} \text{ S cm}^{-1}$)
A	45	56.8	1.26	2.26
B	43	42.9	1.10	1.22
C	46	30.2	0.98	0.79
D	48	82.7	1.52	1.32
E	44	54.8	1.48	1.01
F	46	43.6	1.04	0.82

form membranes. It can be observed that an increase in the imidazole group content in the membrane leads to the increase of IEC. The data in Table 2 shows a clear trend of increasing water uptake with the enhancement of IEC. Membrane D exhibited the highest IEC of 1.52 mmol g^{-1} with water uptake of 82.7%.

The ionic exchange capacity of the membrane can be enhanced by increasing the amount of charged groups in the membrane. However, this usually coincides with a loss of the mechanical properties because of excessive water uptake. Therefore, the water uptake of the membrane should be controlled within a proper range to get optimal performance.

3.4. Ionic conductivity

Ionic conductivity is believed to be a key property for anion exchange membranes applied in alkaline AEMFCs. Table 2 lists the ionic conductivities of the six OH^- form membranes at 30 °C. The ionic conductivities of the six OH^- form membranes as a function of the temperature are shown in Figs. 3 and 4. Membrane A, B and C are based on the copolymer of [VBI]Br and styrene, and Membrane D, E and F are based on the copolymer of [VMI]I and styrene. It is found that at 30 °C the ionic conductivities increase with the increasing content of imidazolium cation groups. This can be explained that the more imidazolium cation groups, the more OH^- charge carriers. Insufficient imidazole functional groups will lower the conductivity of the membrane whereas excess imidazole functional groups will lead to poor dimensional stability and mechanical properties of the membrane.

Membranes exhibit an increment in the ionic conductivity when the temperature continues to increase. The ionic conductivity of membrane A goes from $2.26 \times 10^{-2} \text{ S cm}^{-1}$ to $4.92 \times 10^{-2} \text{ S cm}^{-1}$ while the temperature varies from 30 °C to 80 °C. This can be explained that the ions become more active at a higher

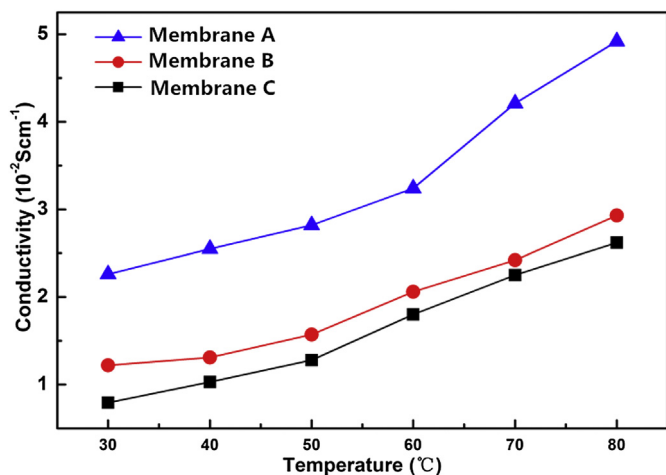


Fig. 3. Ionic conductivities of membrane A, B and C as a function of temperature.

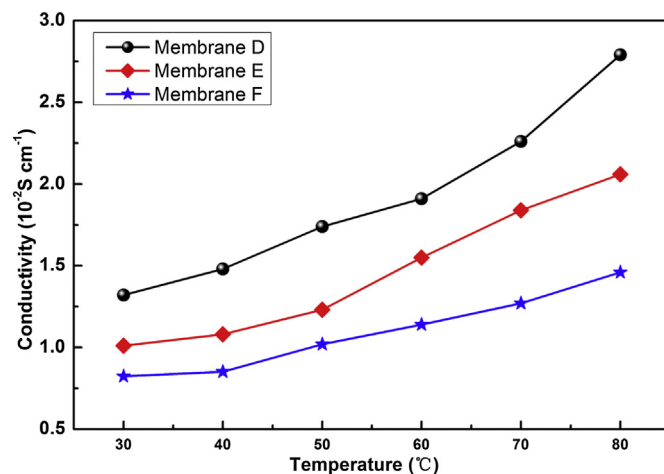


Fig. 4. Ionic conductivities of membrane D, E and F as a function of temperature.

temperature and their migration become faster with increasing temperature. Furthermore, water cluster can offer transport channels for anions inside the anion exchange membrane. The polymeric chain will be more elastic and higher water-absorbing at elevated temperature, result in a more incompact membrane structure, wider anion transferring channels and more ions transfer [25–29]. It can be concluded that the ionic conductivity of OH^- form membranes was mainly determined by two factors, the concentration of charge carriers and the water uptake of membranes. Among these two types of membranes, membrane A and D exhibit the highest ionic conductivity at a given temperature, with higher content of imidazolium cation groups and higher water uptake, respectively.

Fig. 5 is the relationship between $\ln(\sigma)$ and $1000/T$. From Fig. 5, it is also can be found that the temperature dependence of hydroxide conductivity follows the Arrhenius equation. According to the Arrhenius law, the apparent activation energies (E_a) of the membranes were calculated. The E_a value of membrane A and membrane D are $12.765 \text{ kJ mol}^{-1}$ and $11.240 \text{ kJ mol}^{-1}$, respectively.

3.5. Chemical stability and oxidative stability

The chemical stability of anion exchange membranes is

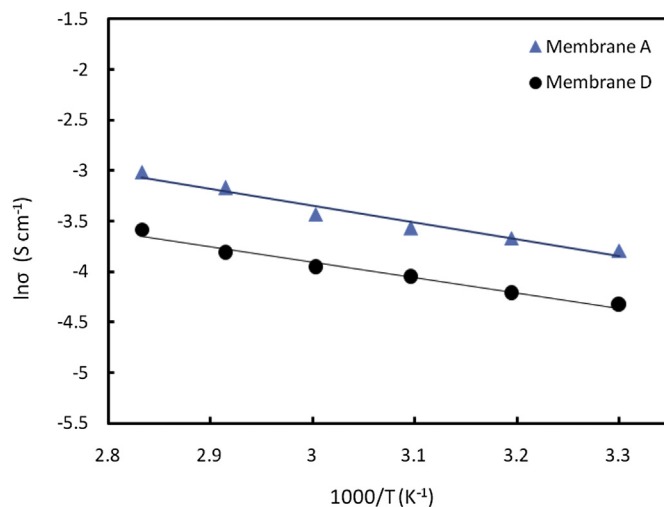


Fig. 5. Arrhenius plots of ionic conductivity for OH^- form anion exchange membranes.

considered to be another key property for alkaline AEMFCs. In order to simulate the working environment of alkaline AEMFCs, the membranes were treated at a relatively high temperature. Also the AEMs were immersed into different concentrations of NaOH solution to examine the durability of the cationic groups in the membranes when suffering constant chemical attack under a high pH conditions. Membrane A and D are used as test subjects in this work, the details about the measurement are described in Section 2.9. Fig. 6 shows the conductivities of ten samples after treated with 2, 4, 6, 8 and 10 mol L⁻¹ NaOH solution at 60 °C for 120 h. The conductivity of membrane A ranged from 2.26 to 2.34 × 10⁻² S cm⁻¹, while that of membrane D ranged from 1.37 to 1.5 × 10⁻² S cm⁻¹. The conductivities slightly increased with the increasing concentration, which can be explained that the portable OH⁻ inside the membranes enhanced under higher pH conditions. Compared with the conductivities of the contrast samples, 2.26 × 10⁻² S cm⁻¹ and 1.37 × 10⁻² S cm⁻¹, there are no significant changes can be observed. The results show that the membranes could tolerate high pH conditions at a temperature up to 60 °C.

It is known that the radical oxidation-induced polymer degradation is one of the main reasons that cause deterioration of ion exchange membranes [30]. So, it is very important to develop anion exchange membranes with good radical oxidative stability. Fenton's reagent is extensively adopted to evaluate the oxidative stability of the membrane for fuel cell applications. In this work, the membrane A and D were soaked in 3% hydrogen peroxide containing 4 ppm FeSO₄ at 80 °C under stirring. Every 24 h, the membrane samples were taken out of the solution and quickly weighed after removing the surface liquid with filter paper. As shown in Fig. 7, the weights of the membranes remain stable within 120 h. This indicates that the developed membranes possess good oxidative stability.

Unlike the quaternary alkyl ammonium cationic groups, a nucleophilic displacement or a Hofmann degradation will not occur on the imidazolium cationic groups under high pH conditions and a relatively high temperature. There is no β hydrogen in the 1,3-alkyl substituted imidazolium cationic groups with a big π bond conjugated system. Therefore, the imidazolium cationic groups could stay stable under high pH conditions. As a result, the membranes prepared in this work showed excellent chemical stability and oxidative stability.

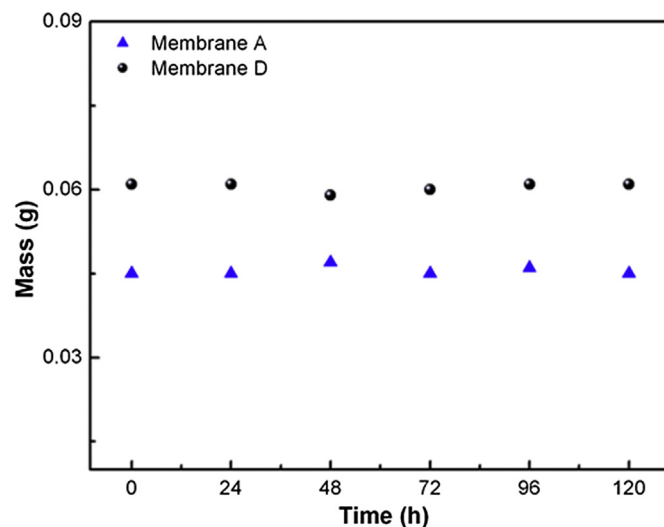


Fig. 7. Mass of membrane A and D after immersed in Fenton's reagent as a function of time.

3.6. Fabrication of MEA and fuel cell test

For the MEA fabrication, the OH⁻ form membrane A was used as the alkaline solid polymer electrolyte membrane due to its higher ion conductivity and better dimensional stability compared with membrane D. The water uptake of membrane D is too high (82.7%) to keep stable dimension of the membrane in high humidity environments, as mentioned in Section 3.3. In order to prepare the ionomer solution, the Cl⁻ in the copolymer should be completely converted to OH⁻, because the Cl⁻ would cause the deactivation of Pt catalyst. A single cell was assembled using Pt catalyst in both anode and cathode. The cell was tested with pure H₂ and O₂ under 100% humidity at 60 °C and ambient pressure. Fig. 8 shows the voltage–current density relationship and the polarization curves of the single cell using membrane A. It is observed that the open circuit voltage (OCV) of the H₂/O₂ fuel cell is 1.07 V, the high OCV indicates that the membrane A is a good barrier between the fuel and oxidant streams [31]. The maximum power density of 116 mW cm⁻² is obtained at a current density of 230 mA cm⁻². The

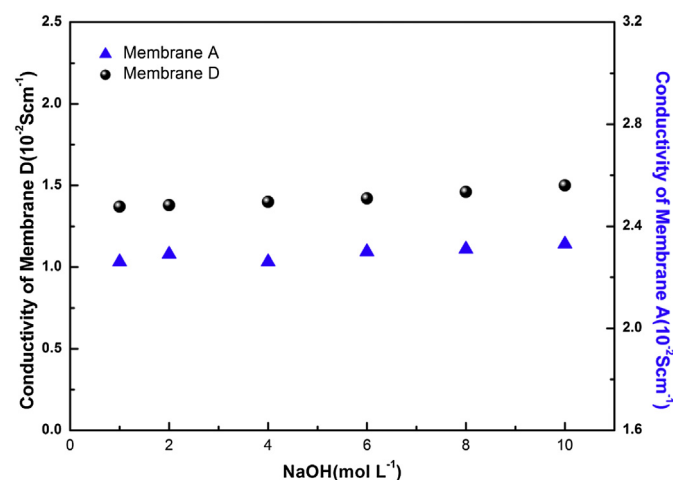


Fig. 6. The conductivities of membrane A and D after treatment with different concentrations of NaOH solution at 60 °C.

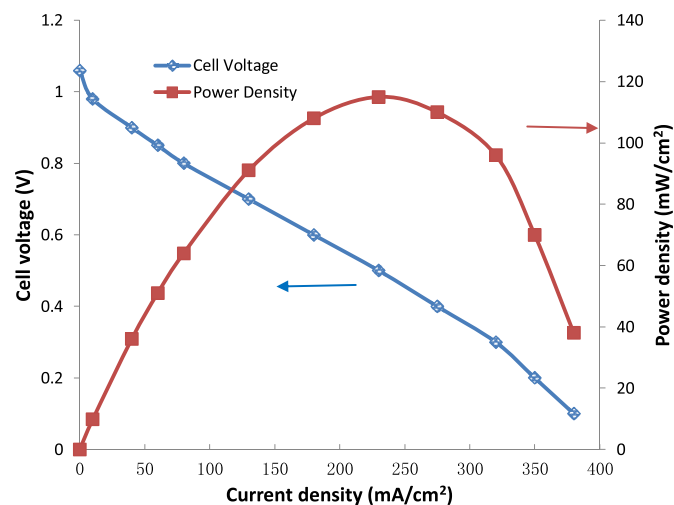


Fig. 8. The voltage–current density relationship and the polarization curves of the H₂/O₂ fuel cell using membrane A at 60 °C.

voltage of the cell reduces gradually with the increasing current density. This is only a primary study on the performance of the H₂/O₂ fuel cell of membrane A. The great efforts should be focused on MEA fabrication and fuel cell testing conditions. There is great potential to improve performance of alkaline AEMFCs.

4. Conclusions

Novel anion exchange membranes based on imidazolium ionic liquids have been successfully prepared via free radical copolymerization and solution-casting method. The synthetic routes of IILs and copolymers have the advantages of simple manufacturing process and low cost, and they are suitable for large-scale industrial productions. The properties of the copolymers could be tuned by varying the monomer ratios in the reactants. The chemical structures of the synthesized IILs and membranes are confirmed by FT-IR. The TGA curves show excellent thermal stability of these membranes and the onset decomposition temperatures are above 200 °C. A appropriate level of water uptake, high ionic exchange capacity and ionic conductivity could be achieved. The water uptake, IEC and ionic conductivity of membrane A are as high as 56.8%, 1.26 mmol g⁻¹ and 2.26×10^{-2} S cm⁻¹ at 30 °C, respectively. The ionic conductivity could be enhanced by raising the temperature, reaching to 4.92×10^{-2} S cm⁻¹ at 80 °C. All the membranes show excellent chemical stability after treated in high pH concentrations of NaOH solution at 60 °C for 120 h. Membrane A is used in the fuel cell test and the open circuit voltage (OCV) of the H₂/O₂ fuel cell is 1.07 V. The power densities of the H₂/O₂ fuel cell attain a peak value of 116 mW cm⁻² at a current density of 230 mA cm⁻² at 60 °C. These results have demonstrated brilliant prospect of the synthesized membranes for alkaline fuel cell applications. Further work to optimize the MEA fabrication and fuel cell testing conditions is in progress.

Acknowledgments

We gratefully acknowledge the High-Tech Research and Development Program of China (No. 2008AA05Z107), and National Nature Science Foundation of China Grant (Nos. 20876129, 21376195 and 21321062) for the financial support of this work.

References

- [1] A. Kirubakaran, S. Jain, R.K. Nema, A review on fuel cell technologies and power electronic interface, *Renew. Sustain. Energy Rev.* 13 (2009) 2430–2440.
- [2] L. Gubler, G.G. Scherer, Trends for fuel cell membrane development, *Desalination* 250 (2010) 1034–1037.
- [3] M.G. Schultz, T. Diehl, G.P. Brasseur, W. Zittel, Air pollution and climate-forcing impacts of a global hydrogen economy, *Science* 302 (2003) 624–627.
- [4] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, Transport properties of ionomer composite membranes for direct methanol fuel cells, *J. Electroanal. Chem.* 532 (2002) 75–83.
- [5] T. Li, Y. Yang, A novel inorganic/organic composite membrane tailored by various organic silane coupling agents for use in direct methanol fuel cells, *J. Power Sources* 187 (2009) 332–340.
- [6] T. Schultz, S. Zhou, K. Sundmacher, Current status of and recent developments in the direct methanol fuel cell, *Chem. Eng. Technol.* 24 (2001) 1223–1233.
- [7] M. Ünü, J. Zhou, P.A. Kohl, Self humidifying hybrid anion-cation membrane fuel cell operated under dry conditions, *Fuel Cells* (2009) 268–275.
- [8] G.F. McLean, T. Niet, S. Prince-Richard, N. Djilali, An assessment of alkaline fuel cell technology, *Int. J. Hydrogen Energy* 27 (2002) 507–526.
- [9] J.R. Varcoe, R.C.T. Slade, G.L. Wright, Y. Chen, Steady-state dc and impedance investigations of H₂/O₂ alkaline membrane fuel cells with commercial Pt/C, Ag/C, and Au/C cathodes, *J. Phys. Chem. B* 110 (2006) 21041–21049.
- [10] D. Tang, J. Pan, S. Lu, L. Zhuang, J. Lu, Alkaline polymer electrolyte fuel cells: principle, challenges, and recent progress, *Sci. China-Chemistry* 53 (2010) 357–364.
- [11] J.S. Spendlow, J.D. Goodpaster, P.J.A. Kenis, A. Wieckowski, Mechanism of CO Oxidation on Pt(111) in alkaline media, *J. Phys. Chem. B* 110 (2006) 9545–9555.
- [12] L. Li, Y.X. Wang, Quaternized polyethersulfone cardo anion exchange membranes for direct methanol alkaline fuel cells, *J. Membr. Sci.* 262 (2005) 1–4.
- [13] J. Fang, P.K. Shen, Quaternized poly (phthalazinone ether sulfone ketone) membrane for anion exchange membrane fuel cells, *J. Membr. Sci.* 285 (2006) 317–322.
- [14] J.S. Park, S.H. Park, S.D. Yim, Y.G. Yoon, W.Y. Lee, C.S. Kim, Performance of solid alkaline fuel cells employing anion-exchange membranes, *J. Power Sources* 178 (2008) 620–625.
- [15] Junfeng Zhou, Murat Unlu, Jose A. Vega, Paul A. Kohl, *J. Power Sources* 190 (2009) 285–292.
- [16] Jun Fang, Yixu Yang, Xiaohuan Lu, Meiling Ye, Wei Li, Yanmei Zhang, Cross-linked, ETFE-derived and radiation grafted membranes for anion exchange membrane fuel cell applications, *Int. J. Hydrogen Energy* 37 (2012) 594–602.
- [17] Y. Luo, J. Guo, Y. Liu, Q. Shao, C. Wang, D. Chu, Copolymerization of methyl methacrylate and vinylbenzyl chloride towards alkaline anion exchange membrane for fuel cell applications, *J. Membr. Sci.* 423–424 (2012) 209–214.
- [18] L. Wu, G. Zhou, X. Liu, Zh Zhang, Ch Li, T. Xu, Environmentally friendly synthesis of alkaline anion exchange membrane for fuel cells via a solvent-free strategy, *J. Membr. Sci.* 371 (2011) 155–162.
- [19] J.R. Varcoe, R.C.T. Slade, Prospects for alkaline anion-exchange membranes in low temperature fuel cells, *Fuel Cells* 5 (2005) 187–200.
- [20] W. Li, J. Fang, M. Lv, C.X. Chen, X.J. Chi, Y.X. Yang, Y.M. Zhang, Novel anion exchange membranes based on polymerizable imidazolium salt for alkaline fuel cell applications, *J. Mater. Chem.* 21 (2011) 11340–11346.
- [21] M. Guo, J. Fang, H. Xu, W. Li, X. Lu, C. Lan, K. Li, Synthesis and characterization of novel anion exchange membranes based on imidazolium-type ionic liquid for alkaline fuel cells, *J. Membr. Sci.* 362 (2010) 97–104.
- [22] H.L. Ngo, K. LeCompte, L. Hargens, A.B. McEwen, Thermal properties of imidazolium ionic liquids, *Thermochim. Acta* 357 (2000) 97–102.
- [23] Y. Ye, Y.A. Elabd, Relative chemical stability of imidazolium-based alkaline anion exchange polymerized ionic liquids, *Macromolecules* 44 (2011) 8494–8503.
- [24] J. Wang, Z. Zhao, F. Gong, S. Li, S. Zhang, Synthesis of soluble poly(arylene ether sulfone) ionomers with pendant quaternary ammonium groups for anion exchange membranes, *Macromolecules* 42 (2009) 8711–8717.
- [25] D.B. Das, V. Nassehi, R.J. Wakeman, A finite volume model for the hydrodynamics of combined free and porous flow in sub-surface regions, *Adv. Environ. Res.* 7 (2002) 35–58.
- [26] J.J. Kang, W.Y. Li, Y. Lin, X.P. Li, X.R. Xiao, S.B. Fang, Synthesis and ionic conductivity of a polysiloxane containing quaternary ammonium groups, *Polym. Adv. Technol.* 15 (2004) 61–64.
- [27] D.S. Kim, G.P. Robertson, M.D. Guiver, Comb-shaped poly(arylene ether sulfone)s as proton exchange membranes, *Macromolecules* 41 (2008) 2126–2134.
- [28] D.S. Kim, G.P. Robertson, Y.S. Kim, M.D. Guiver, Copoly(arylene ether)s containing pendant sulfonic acid groups as proton exchange membranes, *Macromolecules* 42 (2009) 957–963.
- [29] B.P. Tripathi, M. Kumar, V.K. Shahi, Organic-inorganic hybrid alkaline membranes by epoxide ring opening for direct methanol fuel cell applications, *J. Membr. Sci.* 360 (2010) 90–101.
- [30] H. Wang, G.A. Capuano, Behavior of raipore radiation-grafted polymer membranes in H₂/O₂ fuel cells, *J. Electrochem. Soc.* 145 (1998) 780–786.
- [31] Yang Wang, Li Li, Ling Hu, Lin Zhuang, Juntao Lu, Boqing Xu, *Electrochem. Commun.* 5 (2003) 662–666.